

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
26 April 2001 (26.04.2001)

PCT

(10) International Publication Number
WO 01/29167 A1

(51) International Patent Classification⁷: C11D 3/386, 7/02

(21) International Application Number: PCT/US00/28560

(22) International Filing Date: 13 October 2000 (13.10.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/159,711 15 October 1999 (15.10.1999) US

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AT (utility model), AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, CZ (utility model), DE, DE (utility model), DK, DK (utility model), DM, DZ, EE, EE (utility model), ES, FI, FI (utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KR (utility model), KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

- With international search report.
- Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/29167 A1

(54) Title: ENZYMATIC LIQUID CLEANING COMPOSITION EXHIBITING ENHANCED AMYLASE ENZYME STABILITY

(57) Abstract: An aqueous liquid or gel type detergent composition comprises (a) from about 0.1 % to about 15 % by weight, of boric acid or a boron compound; (b) from about 0.1 % to about 10 % by weight, of a polyhydroxy compound selected from the group consisting of ethylene glycol, propylene glycol, 1,2-propanediol, butylene glycol, hexylene glycol, glycerol, mannitol, sorbitol, erythritol, glucose, fructose, lactose, erythritol-1,4-anhydride, and mixtures thereof; and (c) from about 0.01 % to about 1.0 % by weight of a reducing alkali metal salt selected from the group consisting of alkali metal sulphites, alkali metal bisulphites, alkali metal metabisulphites, alkali metal thiosulphates, alkali metal borohydrides, and mixtures thereof; and (d) from about 5 % to about 80 % water. The compositions provide improved stability of amylase enzymes, particularly in the presence of protease enzymes.

ENZYMATIC LIQUID CLEANING COMPOSITION EXHIBITING ENHANCED
AMYLASE ENZYME STABILITY

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TECHNICAL FIELD

The present invention relates to aqueous liquid or gel type detergent compositions. More particularly, the invention relates to aqueous liquid or gel type detergent compositions exhibiting enhanced amylase enzyme stability and a process of enhancing stability of amylase enzymes by using a combination of boric acid or a boron compound capable of forming boric acid in the composition, a polyhydroxy compound, preferably propanediol, and a very low level of a reducing alkali metal salt, preferably an alkali metal sulfite.

BACKGROUND OF THE INVENTION

Aqueous liquid enzymatic detergent compositions are well known in the art. The major problem encountered with such compositions is that of ensuring a sufficient storage stability of the enzymes in these compositions.

It is desirable to enhance the stability of amylase enzymes, particularly in the presence of protease enzymes which can degrade amylases, in aqueous liquid or gel type detergent compositions. High-alkaline amylases, such as alpha amylases are described in British Specification No. 1,296,839, assigned to Novo, incorporated herein by reference. The use of an enzyme stabilizing system comprising a mixture of boric acid or an alkali metal borate with a polyol or a polyfunctional amino compound, together with a certain high level of a reducing alkali metal salt such as sodium sulphite, is known and disclosed in U.S. Patent 4,462,922, incorporated herein by reference.

However, it has been desirable to attain enzyme stability using lower levels of propanediol and very low levels of alkali metal sulfites. It has also been desirable to use boric acid rather than alkali metal borates and still obtain a high degree of enzyme stability. It has been desirable to use low levels of boric acid, propanediol and alkali metal sulphite because a low level of these components helps improve the translucency and transparency of the liquid or gel detergent composition. However, in the past it has been understood that low levels of one or more of the aforementioned boric acid, diol and alkali metal sulphite may not provide adequate enzyme stability. The present invention

utilizes low levels of the aforementioned components in combination while surprisingly enhancing enzyme stability.

The present invention is thus directed to overcome one or more of the problems as set forth before.

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BACKGROUND ART

U.S. Patent No. 4,462,922, issued to Boskamp, Jelles V., and assigned to Lever Brothers Company, discloses an enzyme stabilizing system comprising a mixture of boric acid or an alkali metal borate with a polyol or a polyfunctional amino compound, together with a certain level of a reducing alkali metal salt such as sodium sulphite.

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U.S. Patent No. 4,404,115, issued to Tai, Ho T., and assigned to Lever Brothers Company, discloses an enzymatic liquid cleaning composition, comprising an enzyme stabilizing system including an alkali metal borate, alkali metal sulphite and a polyol.

SUMMARY OF THE INVENTION

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The invention meets the needs above by providing an aqueous liquid or gel type detergent composition, an aqueous enzymatic liquid or gel detergent composition containing an amylase enzyme, and a process for stabilizing an amylase enzyme in an aqueous enzymatic liquid or gel detergent composition. Such detergent compositions are useful for cleaning tableware (i.e., glassware, china, silverware, plastic, etc.), kitchenware, household surfaces such as floors, bathroom fixtures and countertops, and fabrics. The compositions may be fully formulated cleaning products or they may be additive or specialty products that can be used alone or with other cleaning products. Particularly preferred compositions herein are for use in automatic dishwashing machines.

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In one aspect of the present invention, an aqueous liquid or gel type detergent composition comprises (a) from about 0.1% to about 15% by weight of boric acid or a boron compound capable of forming boric acid in the composition; (b) from about 0.1% to about 10% by weight of a polyhydroxy compound selected from the group consisting of ethylene glycol, propylene glycol, 1,2-propanediol, butylene glycol, hexylene glycol, glycerol, mannitol, sorbitol, erythritol, glucose, fructose, lactose, erythritol-1,4-anhydride, and mixtures thereof; and (c) from about 0.01% to about 1.0% by weight of a reducing alkali metal salt selected from the group consisting of alkali metal sulphites,

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alkali metal bisulphites, alkali metal metabisulphites, alkali metal thiosulphates, alkali metal borohydrides, and mixtures thereof; and (d) from about 5% to about 80% water.

In another aspect of the present invention, an aqueous enzymatic liquid or gel type detergent composition comprises an amylase enzyme, an enzyme stabilizing system, and water. The enzyme stabilizing system comprises (a) from about 0.1% to about 15% by weight of the composition, of boric acid or a boron compound capable of forming boric acid in the composition; (b) from about 0.1% to about 10% by weight of the composition, of a polyhydroxy compound selected from the group consisting of ethylene glycol, propylene glycol, 1,2-propanediol, butylene glycol, hexylene glycol, glycerol, mannitol, sorbitol, erythritol, glucose, fructose, lactose, erythritol-1,4-anhydride, and mixtures thereof; and (c) from about 0.01% to about 1.0% by weight of the composition, of a reducing alkali metal salt selected from the group consisting of alkali metal sulphites, alkali metal bisulphites, alkali metal metabisulphites, alkali metal thiosulphates, alkali metal borohydrides, and mixtures thereof.

In yet another aspect of the present invention, a process for stabilizing an amylase enzyme in an aqueous enzymatic liquid or gel type detergent composition comprises mixing (a) from about 0.1% to about 15% by weight of the composition, of boric acid or a boron compound capable of forming boric acid in the composition; (b) from about 0.1% to about 10% by weight of the composition, of a polyhydroxy compound selected from the group consisting of ethylene glycol, propylene glycol, 1,2-propanediol, butylene glycol, hexylene glycol, glycerol, mannitol, sorbitol, erythritol, glucose, fructose, lactose, erythritol-1,4-anhydride, and mixtures thereof; and (c) from about 0.01% to about 1.0% by weight of the composition of a reducing alkali metal salt selected from the group consisting of alkali metal sulphites, alkali metal bisulphites, alkali metal metabisulphites, alkali metal thiosulphates, alkali metal borohydrides, and mixtures thereof; with detergent ingredients including an amylase enzyme.

DETAILED DESCRIPTION OF THE INVENTION

In the preferred embodiment of the present invention, an aqueous liquid or gel type detergent composition comprises (a) from about 0.1% to about 15% by weight, of boric acid or a boron compound capable of forming boric acid in the composition; (b) from about 0.1% to about 10% by weight, of a polyhydroxy compound selected from the

group consisting of ethylene glycol, propylene glycol, 1,2-propanediol, butylene glycol, hexylene glycol, glycerol, mannitol, sorbitol, erythritol, glucose, fructose, lactose, erythritol-1,4-anhydride, and mixtures thereof; and (c) from about 0.01% to about 1.0% by weight of a reducing alkali metal salt selected from the group consisting of alkali metal sulphites, alkali metal bisulphites, alkali metal metabisulphites, alkali metal thiosulphates, alkali metal borohydrides, and mixtures thereof; and (d) from about 5% to about 80%, preferably from about 20% to about 80%, more preferably from about 40% to about 70%, by weight of water.

In the preferred embodiment, the boric acid or boron compound capable of forming boric acid in the composition is desirably present in an amount from about 0.5% to about 10% by weight, preferably from about 1% to about 5%, and more preferably from about 2% to about 4% by weight (calculated on the basis of boric acid present). Boric acid is particularly preferred herein, although other compounds such as boric oxide, borax and other alkali metal borates (e.g., sodium ortho-, meta-, and pyroborate, and sodium pentaborate) are suitable. Substituted boric acids (e.g., phenylboronic acid, butane boronic acid, and p-bromo phenylboronic acid) can also be used in place of boric acid.

The compositions of the present invention also contain a polyhydroxy compound as described above. The polyhydroxy compound preferably contains from 2 to 6 carbon atoms and from 2 to 6 hydroxy groups, and is preferably selected from propylene glycol, ethylene glycol, glycerol, sorbitol, and glucose, and mixtures thereof. The polyhydroxy compound is preferably 1,2-propanediol. In a preferred embodiment, the polyhydroxy compound is desirably present in an amount from about 0.1% to about 7% by weight, preferably from about 0.1% to about 5% by weight, and more preferably from about 0.1% to about 1% by weight. Most preferably, the polyhydroxy compound is present at a level of from about 0.2% to about 1% by weight.

The compositions of the present invention also contain from about 0.01% to about 1.0%, preferably from about 0.01% to about 0.5%, by weight of a reducing alkali metal salt selected from the group consisting of alkali metal sulphites, bisulphites, metabisulphites, thiosulphates, and borohydrides, and mixtures thereof. In the preferred embodiment, the reducing salt is an alkali metal sulphite which is desirably present in an

amount from about 0.01% to about 0.5% by weight, and preferably from about 0.01% to about 0.1% by weight. The preferred alkali metal sulphite is sodium sulphite.

In the present invention, it has most surprisingly been found that contrary to the teachings of the art in this field of endeavor, using low levels of alkali metal sulfites in combination with the aforementioned levels of boric acid or boron compound and polyhydroxy compound such as propanediol, results in a better enzyme stabilizing formulation which is very effective in stabilizing amylases such as Termamyl and Duramyl, particularly in the presence of proteases which are known to degrade amylases, as compared to an enzyme stabilizing formulation that contains no sulphites at all. This is indeed a surprising discovery and claimed henceforth in this invention.

Thus, in one aspect of the present invention, the liquid or gel detergent composition also contains an amylase enzyme. Amylases suitable herein, especially for but not limited to automatic dishwashing purposes, include for example α -amylases described in GB 1,296,839 to Novo, and especially TERMAMYL[®], available from Novo. FUNGAMYL[®] from Novo is also useful herein. Engineering of enzymes for improved stability, e.g., oxidative stability, is known. See, for example, J. Biological Chem., Vol. 260, No. 11, June 1985, pp 6518-6521. Preferred amylases include those according to the WO 9402597, Novo, Feb. 3, 1994, incorporated herein by reference. Other amylases include variants having additional modification as described in WO 9510603 A, incorporated herein by reference, and are available from Novo as DURAMYL[®]. Other particularly preferred oxidative stability enhanced amylases include those described in WO 9418314 to Genencor International and WO 9402597 to Novo, both incorporated by reference.

The compositions of the present invention also preferably contain protease enzymes to enhance cleaning performance. The enzyme stabilizing system herein is particularly effective at stabilizing amylases in the presence of proteases which are known to degrade enzymes.

The preparation of protease enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE[®] and SAVINASE[®] from Novo, as well as Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9,

1985. See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 9318140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 9203529 A to Novo. Other preferred proteases include those of WO 9510591 A to Procter & Gamble. When
5 desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 9507791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 9425583 to Novo.

Enzymes are normally incorporated into detergent or detergent additive compositions at levels sufficient to provide a "cleaning-effective amount". The term
10 "cleaning effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates, such as dishware and the like. In practical terms for current commercial preparations, the compositions herein may comprise from about 0.01% to about 5%, preferably about 0.1% to about 2% by weight of a commercial enzyme preparation.
15 Protease enzymes are present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Other detergent ingredients

The compositions of the invention may also contain additional components generally found in detergent compositions. The compositions may contain surfactants,
20 especially anionic and/or nonionic surfactants, solvents, clay, polycarboxylate thickeners, baking soda, brighteners, carbonates, phosphates, dicarboxylic acid, siloxanes, perfumes, bleach and bleach catalysts, and mixtures thereof. Preferred components are discussed in more detail hereafter.

(a) Thickeners

25 The physical stability of the liquid or gel product may be improved, and the thickness of the product may be altered, by the addition of a cross-linking thickener to the liquid or gel detergent product as a thixotropic thickener.

Thickeners for use herein include those selected from clay, polycarboxylates, such as Polygel®, gums, carboxymethyl cellulose, polyacrylates, and mixtures thereof. The
30 preferred clay type herein has a double-layer structure. The clay may be naturally occurring, e.g., Bentonites, or artificially made, e.g., Laponite®. Laponite® is supplied by

Southern Clay Products, Inc. See *The Chemistry and Physics of Clays*, Grimshaw, 4th ed., 1971, pages 138-155, Wiley-Interscience.

(b) PH adjusting components

The above liquid or gel detergent product is preferably low foaming, readily
5 soluble in the washing medium and most effective at pH values best conducive to
improved cleaning performance, such as in a range of desirably from about pH 6.5 to
about pH 12.5, and preferably from about pH 7.0 to about pH 12.0, more preferably from
about pH 8.0 to about pH 12.0. Preferably the pH is less than about 10.0 for better
enzyme stability, most preferably less than about 9.0. The pH adjusting components are
10 desirably selected from sodium or potassium hydroxide, sodium or potassium carbonate
or sesquicarbonate, sodium or potassium silicate, boric acid, sodium or potassium
bicarbonate, sodium or potassium borate, and mixtures thereof. NaOH or KOH are the
preferred ingredients for increasing the pH to within the above ranges. Other preferred
pH adjusting ingredients are sodium carbonate, potassium carbonate, and mixtures
15 thereof.

(c) Low Foaming Surfactant

Non-chlorine bleach-containing liquid ADW compositions of the present
invention preferably contain a nonionic surfactant, preferably an alkyl ethoxylate
surfactant. One example of a non-chlorine bleach stable surfactant is SLF18®
20 manufactured by BASF Corporation. Alternatively, in chlorine bleach-containing liquid
ADW compositions, chlorine bleach stable low foaming surfactants are preferred, and
such surfactants are present in a range of from about 0.1% to about 10% by weight of the
liquid composition. Such surfactants are generally known to one skilled in the art and
need not be elaborated here, for purposes of brevity. An example of a chlorine bleach
25 stable surfactant is Dowfax® anionic surfactant available from the Dow Chemical
Company. Surfactants useful herein are described in more detail in WO 98/03622,
published January 29, 1998, incorporated herein by reference.

(d) Builder

The compositions of the present invention also preferably contain one or more
30 detergent builders to assist in controlling mineral hardness and in the removal of
particulate soils. Inorganic as well as organic builders can be used.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least about 1% builder. Liquid formulations typically comprise from about 5% to about 50%, more typically about 5% to about 30%, by weight, of detergent builder.

5 Lower or higher levels of builder, however, are not meant to be excluded.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and

10 aluminosilicates.

Examples of silicate builders are the alkali metal silicates, particularly those having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst

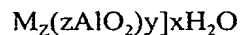
15 (commonly abbreviated herein as "SKS-6"). NaSKS-6 can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. Other layered silicates, such as those having the general formula $\text{NaMSi}_x\text{O}_{2x+1} \cdot y\text{H}_2\text{O}$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20 can be used herein. Various other layered silicates from Hoechst include NaSKS-5,

20 NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders may be useful in the present invention. Aluminosilicate

25 builders include those having the empirical formula:

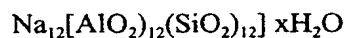


wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. A

30 method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations

Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites ($x = 0 - 10$) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of importance for liquid detergent formulations due to their availability from renewable resources and their biodegradability. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

5 Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity.

(e) Other adjunct detergent ingredients

10 The liquid or gel detergent composition may optionally contain up to about 20% of a dispersant polymer selected from the group consisting of polyacrylates and polyacrylate copolymers.

The compositions of the present invention may also contain other enzymes and enzyme stabilizing agents such as calcium ion and short chain carboxylic acids as disclosed in U.S. Patent 4,537,707, Severson, and U.S. Patent 4,318,818, Letton, et. al., both incorporated herein by reference.

15 The compositions herein may also contain bleaching agents and activators, material care agents, and chelating agents such as disclosed in WO 98/03622, incorporated herein by reference.

20 To exemplify an embodiment of the present invention and demonstrate its benefits, Formula B, an embodiment of the present invention having 0.1% by weight sodium sulphite, is compared with Formula A which has 0% sulphite, and Formula C which also has 0% sulfite and a higher level of boric acid and 1,2 propanediol, in Table 1. A comparison of the amylase stability is shown in Table 2.

Table 1

Ingredients (active)	Formula A	Formula B	Formula C
Sodium Tripolyphosphate	16	16	16
K ₂ SO ₄	16	16	16
Boric Acid	3.0	3.0	4.0
1,2 propanediol	0.5	0.5	6.0
Sodium sulfite	0	0.1	0
CaCl ₂ ·2H ₂ O	0.037	0.037	0.037
Nonionic surfactant (SLF18)	0.5	0.5	0.5
Protease (4% active)	0.5	0.5	0.5
Amylase (4% active) (Termanyl)	0.27	0.27	0.27
Polyacrylate thickener (Polygel DKP)	1.22	1.22	1.22
Perfume	0.10	0.10	0.10
Dye	0.0016	0.0016	0.0016
Deionized water	BAL	BAL	BAL
(pH at 1% in water)	(8.5)	(8.5)	(8.5)

Table 2

5

% amylase remaining @ 80°F (26.7°C)	Formula A	Formula B	Formula C
after 7 days	63	93	80
after 14 days	36	93	56
after 28 days	34	88	53
after 42 days	29	91	46

As can be seen above, Formula B containing 0.1% sodium sulfite has significantly better amylase stability than Formula A containing no sulfite and Formula C containing no sulfite but higher levels of boric acid and 1,2 propanediol.

10

Other compositions of the present invention are as follows:

Table 3

Ingredients (active)	Formula D	Formula E
Sodium Tripolyphosphate	22.0	
Sodium citrate		20.0
KOH	4.6	4.6
H ₂ SO ₄	3.9	3.9
Boric Acid	3.0	2.0
1,2 propanediol	0.5	2.0
Sodium sulfite	0.1	0.2
CaCl ₂ ·2H ₂ O	0.22	0.037
Nonionic surfactant (SLF18)	1.0	3.5
Protease (3.4% active)	0.6	0.6
Amylase (4% active) (Duramyl 300L)	0.27	0.5
Polyacrylate thickener (Polygel DKP)	1.18	1.18
Perfume	0.10	0.10
Deionized water & minors	BAL	BAL
(pH at 1% in water)	(9.6)	

Accordingly, having thus described the invention in detail, it will be obvious to
5 those skilled in the art that various changes may be made without departing from the
scope of the invention and the invention is not to be considered limited to what is
described in the specification.

What is claimed is:

1. An aqueous liquid or gel type detergent composition characterized in that it comprises:
 - (a) from 0.1% to 15% by weight of boric acid or a boron compound capable of forming boric acid in the composition;
 - (b) from 0.1% to 10% by weight of a polyhydroxy compound selected from the group consisting of ethylene glycol, propylene glycol, 1,2-propanediol, butylene glycol, hexylene glycol, glycerol, mannitol, sorbitol, erythritol, glucose, fructose, lactose, erythritol-1,4-anhydride, and mixtures thereof;
 - (c) from 0.01% to 1.0% by weight of a reducing alkali metal salt selected from the group consisting of alkali metal sulphites, alkali metal bisulphites, alkali metal metabisulphites, alkali metal thiosulphates, alkali metal borohydrides, and mixtures thereof; and
 - (d) from 5% to 80% water.
2. The detergent composition according to claim 1, comprising from 0.5% to 10%, preferably from 1% to 5%, by weight of boric acid.
3. The detergent composition according to claim 1 or 2, wherein said polyhydroxy compound is 1,2-propanediol.
4. The detergent composition according to any one of the preceding claims, comprising from 0.1% to 7% by weight of said polyhydroxy compound.
5. The detergent composition according to any one of the preceding claims, comprising from 0.01% to 0.5% by weight of an alkali metal sulphite, preferably sodium sulphite.
6. An aqueous enzymatic liquid or gel type detergent composition characterized in that it comprises:
 - (a) an amylase enzyme;
 - (b) an enzyme stabilizing system comprising:

- (i) from 0.1% to 15% by weight of the composition, of boric acid or a boron compound capable of forming boric acid in the composition;
 - (ii) from 0.1% to 10% by weight of the composition, of a polyhydroxy compound selected from the group consisting of ethylene glycol, propylene glycol, 1,2-propanediol, butylene glycol, hexylene glycol, glycerol, mannitol, sorbitol, erythritol, glucose, fructose, lactose, erythritol-1,4-anhydride, and mixtures thereof; and
 - (iii) from 0.01% to 1.0% by weight of the composition, of a reducing alkali metal salt selected from the group consisting of alkali metal sulphites, alkali metal bisulphites, alkali metal metabisulphites, alkali metal thiosulphates, alkali metal borohydrides, and mixtures thereof; and
- (c) from 5% to 80% water.

7. The detergent composition according to claim 6 comprising from 1% to 5% by weight of boric acid.
8. The detergent composition according to claim 6 or 7 comprising from 0.1% to 7% by weight of the polyhydroxy compound, preferably 1,2-propanediol.
9. The detergent composition according to claim 6, 7 or 8 comprising from 0.01% to 0.5% by weight of an alkali metal sulphite, preferably sodium sulphite.
10. The detergent composition according to any one of the preceding claims comprising from 0.1% to 2% by weight of amylase enzyme and from 0.1% to 2% by weight of protease enzyme.
11. A process for stabilizing an amylase enzyme in an aqueous enzymatic liquid or gel type detergent composition, characterized in that it comprises mixing, with detergent ingredients including an amylase enzyme:
- (i) from 0.1% to 15% by weight of the composition, of boric acid or a boron compound capable of forming boric acid in the composition;

- (ii) from 0.1% to 10% by weight of the composition, of a polyhydroxy compound selected from the group consisting of ethylene glycol, propylene glycol, 1,2-propanediol, butylene glycol, hexylene glycol, glycerol, mannitol, sorbitol, erythritol, glucose, fructose, lactose, erythritol-1,4-anhydride, and mixtures thereof; and
- (iii) from 0.01% to 1.0% by weight of the composition, of a reducing alkali metal salt selected from the group consisting of alkali metal sulphites, alkali metal bisulphites, alkali metal metabisulphites, alkali metal thiosulphates, alkali metal borohydrides, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/US 00/28560

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/386 C11D7/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP 0 533 239 A (UNILEVER PLC ; UNILEVER NV (NL)) 24 March 1993 (1993-03-24) claims 1-8; examples I-II ---	1,4-6, 9-11
A	WO 93 21299 A (PROCTER & GAMBLE) 28 October 1993 (1993-10-28) claims 1-8; examples I-IV ---	1-4,6-8, 10
A	WO 92 19709 A (PROCTER & GAMBLE) 12 November 1992 (1992-11-12) claims 1-4; examples 4,12 ---	1-4
A	WO 99 10466 A (RAI SAROJ ; BARNABAS MARY VIJAYARANI (US); PROCTER & GAMBLE (US); W) 4 March 1999 (1999-03-04) examples 10-12 --- -/--	1-4,6-8

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

9 February 2001

Date of mailing of the international search report

19/02/2001

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/28560

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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